Consumer and Corporate Affairs Canada / Consommation et Corporations Canada
Bureau des brevets / Patent Office
Ottawa, Canada
K1A 0C9

(21) (A1) 2,057,425
(22) 1991/12/11
(43) 1992/06/15

5,046,6/62

(51) INTL.CL.[5] B01D-017/05

(19) (CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Breaking of Water-in-Oil Emulsions

(72) Augustin, Thomas - Germany (Federal Republic of) ;
Kehlenbach, Rolf - Germany (Federal Republic of) ;

(73) Bayer Aktiengesellschaft - Germany (Federal Republic of) ;

(30) (DE) P 40 40 022.0 1990/12/14

(57) 9 Claims

Notice: The specification contained herein as filed

Canada

Breaking of water-in-oil emulsions

Abstract

Water-in-oil emulsions which are the oily phase of an oil-in-water emulsion which has undergone primary breaking are dehydrated by using polymers and/or oligomers of ethylene oxide and/or 1,2-propylene oxide, oxyalkylated phenolic resins, block polymers or copolymers of ethylene oxide and 1,2-propylene oxide crosslinked with diisocyanates, dicarboxylic acids, formaldehyde and/or diglycidyl ethers, polyether-urethanes and/or alkylbenzenesulphonic acid salts as the breaker. The oily phases mentioned are easier to reprocess and/or can be used as fuel.

The present invention relates to a process for the breaking of water-in-oil emulsions which are the oily phase separated off from a previously broken oil-in-water emulsion. In the following text, the breaking of the oil-in-water emulsion is also called primary breaking and the breaking of the resulting oily phase is called secondary breaking.

Various processes and corresponding organic and inorganic breakers are known for primary breaking of oil-in-water emulsions. A water-soluble polymer is often employed for the primary breaking, cationic products in general being preferable to anionic and nonionic products.

Examples of primary breakers are:
synthetic polymers based on acrylamide, pure polyacrylamide being nonionic, copolymers of acrylamide and acrylate being anionic and copolymers of acrylamide and cationic monomers or oligomers being cationic (see, for example, US-A 3,585,148, US-A 4,699,951, DE-A 2,345,922 and DE-A 2,926,103), and furthermore

synthetic polymers based on polyamines and polyamidoamines, as well as quaternised polyamines and quaternised polyamidoamines (see, for example, DE-A 2,262,284, JA-OS (Japanese Published Specification) 20,929-66, US-A 3,915,904, DE-A 2,638,516, US-A 4,287,331, French Patent Specification 1,449,204, US-A 4,575,527, DE-A 2,156,215

and DE-A 2,351,754), and furthermore

homopolymers of dimethyldiallylammonium chloride, also called DADMAC (see, for example, EP-A 0,186,029) and

inorganic breakers, such as inorganic metal salts, for example of magnesium, sodium, calcium, iron, silicon, aluminium and cerium, which can be employed in the form of hydroxides, oxides, chlorides or sulphates. In accordance with the Schulze-Hardy rule, di- and trivalent salts are preferably employed here (see Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd edition, Volume 10, 489, New York 1980).

In the primary breaking, the oily phase is as a rule obtained in the form of a flotation product which creams on the aqueous phase and is in general a water-in-oil emulsion. This can be removed mechanically from the surface of the liquid in a simple manner and then passed for secondary breaking.

A secondary breaking is in general advantageous if the oily phase separated off from the waste oil-in-water emulsion is to be disposed of, for example by working up, dumping or burning. It is then advantageous if this oily phase contains as little water as possible.

For breaking of crude oil emulsions which are water-in-oil emulsions, it is known that block polymers of ethylene oxide and/or 1,2-propylene oxide (see US-A

2,964,478), oxyalkylated phenolic resins (see US-A 2,499,370 and US-A 2,499,368) and block polymers or copolymers of ethylene oxide and 1,2-propylene oxide crosslinked with diisocyanates, dicarboxylic acids, formaldehyde and/or diglycidyl ethers (see EP-A 55,433 and 55,434 and US-A 4,029,708) and polyether-urethanes (see DE-A 3,706,151) can be employed as breakers.

The secondary breaking to be carried out according to the invention, that is to say the breaking of a water-in-oil emulsion which can be the oily phase from the breaking of an oil-in-water emulsion, cannot be compared with the breaking of a crude oil emulsion, because the water-in-oil emulsions which arise in crude oil production are highly stabilised by specific natural emulsifiers. The breakers employed for the breaking of crude oil emulsions have been designed specifically for this breaking. In the emulsion breaking according to the invention, the emulsions to be broken contain no stabilisers or completely different stabilisers from crude oil emulsions.

Breakers which are known for the breaking of crude oil emulsions therefore cannot be applied to secondary breaking of oily phases which originate from breaking of an oil-in-water emulsion.

A process has now been found for the breaking of water-in-oil emulsions which have been obtained from the breaking of oil-in-water emulsions, which is

characterised in that polymers and/or oligomers of ethylene oxide and/or 1,2-propylene oxide, oxyalkylated phenolic resins, block polymers or copolymers of ethylene oxide and 1,2-propylene oxide crosslinked with diisocyanates, dicarboxylic acids, formaldehyde and/or diglycidyl ethers, polyether-urethanes and/or alkylbenzenesulphonic acid salts are employed as the breakers.

Polymers of ethylene oxide and/or 1,2-propylene oxide which are suitable for the process according to the invention can be obtained, for example, by polyalkoxylation of lower alcohols, such as methanol, ethanol, propanols, butanols, pentanols or hexanols, with ethylene oxide and/or 1,2-propylene oxide. Possible alcohols here are also di- and polyols, for example propanediols, butanediols, neopentylglycol, other pentanediols, adipol, hexanediols, cyclohexanediols, 1,4-dihydroxymethylcyclohexane, perhydrobisphenol A, glycerol, trimethylolethane, trimethylolpropane, other hexanetriols and pentaerythritol. Lower amines, for example ethylenediamine and diethylenetriamine, can also be polyoxyalkylated with ethylene oxide and/or 1,2-propylene oxide in order to obtain polymers which are suitable for the present invention. Both block polymers and polymers having a random distribution of different oxyalkyl groups, so-called copolymers, or also mixed forms of these two possibilities, can be used according to the invention. Block polymers of ethylene oxide and 1,2-propylene oxide and those products in which alcohols are first reacted

with a mixture of propylene oxide and 70 to 90% by weight of the total amount of the ethylene oxide to give copolymers, and the remaining 10 to 30% by weight of the ethylene oxide is then introduced, so that a polyether which contains practically only primary OH end groups is formed are preferred. Polymers of ethylene oxide and 1,2-propylene oxide which contain 40 to 60% by weight of ethylene, based on the sum of ethylene oxide + 1,2-propylene oxide, are preferred. Particularly preferred polyethers are built up from the same amounts by weight of ethylene oxide and 1,2-propylene oxide. Polyethers having molecular weights of 600 to 6000, particularly preferably those having molecular weights of 1000 to 5000, are furthermore preferred.

Oxyalkylated phenolic resins which are suitable for the process according to the invention can be obtained, for example, by condensation of alkylphenols with formaldehyde, formalin solution or paraformaldehyde and subsequent alkoxylation.

Block polymers or copolymers of ethylene oxide and/or 1,2-propylene oxide which are crosslinked with diisocyanates, dicarboxylic acids, formaldehyde and/or diglycidyl ethers and are suitable for the process according to the invention can be obtained, for example, if a difunctional polyether consisting of, for example, 30 to 90 parts by weight of 1,2-propylene oxide and 70 to 10 parts by weight of ethylene oxide and having a molecular weight of 2000 to 20,000 is reacted with a bifunctional isocyanate,

a bifunctional carboxylic acid, formaldehyde and/or a bifunctional glycidyl ether. Examples of suitable diisocyanates are hexamethylene diisocyanate, cyclohexane 1,4-diisocyanate, toluylene 2,4- and 2,6-diisocyanate and mixtures thereof, 1-isocyanatomethyl-5-isocyanato-1,3,3-trimethylcyclohexane, 2,2,4- and 2,4,4-trimethylhexamethylene 1,6-diisocyanate, naphthalene 1,5-diisocyanate, cyclopentylene 1,3-diisocyanate, m- and p-phenylene diisocyanate, xylylene 1,3- and 1,4-diisocyanate, 3,3'-dimethyl-diphenylmethane 4,4'-diisocyanate, diphenylmethane 4,4'-diisocyanate, 3,3'-dimethyl-biphenylene 4,4'-diisocyanate, biphenylene 4,4'-diisocyanate, durene diisocyanate, 1-phenoxy-phenylene 2,4'-diisocyanate, 1-tert.-butyl-phenylene 2,4-diisocyanate, methylene-bis-cyclohexyl 4,4'-diisocyanate, 1-chloro-phenylene 2,4-diisocyanate and diphenyl ether 4,4'-diisocyanate. Examples of suitable bisglycidyl ethers are bisglycidyl ethers of bisphenol A, reaction products of bisphenol A and epichlorohydrin, reaction products of epichlorohydrin and aniline and reaction products of perhydrophthalic acid with epichlorohydrin. Examples of suitable difunctional carboxylic acids are oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, maleic acid, fumaric acid and higher saturated or unsaturated dicarboxylic acids.

Examples of crosslinked block polymers or copolymers of ethylene oxide and/or 1,2-propylene oxide which are suitable for the process according to the invention are linked and amine-modified polyalkylene oxides of the

general formula (I)

$$
\begin{array}{l}
NH-CHR-(CH_2)_x-CHR-[-OCHR-(CH_2)_x-CHR-]_y-(OCHR-CHR)_y-O-Q-A \\
| \\
M \\
| \\
NH-CHR-(CH_2)_x-CHR-[-OCHR-(CH_2)_x-CHR-]_y-(OCHR-CHR)_y-O-Q-A
\end{array}
$$

(I)

in which

each R independently denotes hydrogen or a C_1-C_{20}-alkyl radical,

each x independently denotes zero or an integer from 1 to 12,

each y independently denotes zero or an integer from 1 to 120,

each Q independently denotes a C_6-C_{18}-arylene, C_7-C_{18}-aralkylene or C_2-C_{18}-alkylene group,

each A independently denotes hydrogen, hydroxyl or a radical of the formula (II)

$$-(OCHR-CHR)_y-[-OCHR-(CH_2)_x-CHR-]_y-OCHR-(CH_2)_x-CHR-NH_2$$

(II)

where R, x and Y are as defined above, and

M denotes the radical of a diisocyanate, a bisepoxide, a dicarboxylic acid, a dicarboxylic acid dihalide, a biscarboxylic acid anhydride, a diester or a dihalogen compound, after the two reactive groups in each case have reacted with an amine hydrogen atom.

Preferred crosslinked block polymers and/or copolymers of ethylene oxide and/or 1,2-propylene oxide can be obtained by reacting monofunctional polymers of ethylene oxide and/or 1,2-propylene oxide with diisocyanates, bisglycidyl ethers or dicarboxylic acids, for example those described above, and then reacting the products with a polyalkylenepolyamine.

Examples of polyether-urethanes which are suitable for the process according to the invention are urea-modified polyether-urethanes of the formula (III)

$$
\begin{array}{l}
NH\text{-}CO\text{-}NH\text{-}R_3\text{-}[\text{-}NH\text{-}CO\text{-}O\text{-}(CHR_6\text{-}CHR_7O)_x\text{-}(CHR_8\text{-}CHR_9\text{-}O)_y\text{-}R_{10}]_m \\
| \\
R_1 \\
| \\
N\text{-}CO\text{-}NH\text{-}R_4\text{-}[\text{-}NH\text{-}CO\text{-}O\text{-}(CHR_6\text{-}CHR_7O)_x\text{-}(CHR_8\text{-}CHR_9\text{-}O)_y\text{-}R_{10}]_m \\
| \\
R_2 \\
| \\
NH\text{-}CO\text{-}NH\text{-}R_5\text{-}[\text{-}NH\text{-}CO\text{-}O\text{-}(CHR_6\text{-}CHR_7O)_x\text{-}(CHR_8\text{-}CHR_9\text{-}O)_y\text{-}R_{10}]_m
\end{array}
$$

(III)

in which

R_1 and R_2 independently of one another denote C_2-C_{14}-cycloalkylene,

R_3, R_4 and R_5 independently of one another denote optionally substituted alkylene, cycloalkylene or arylene,

R_6, R_7, R_8 and R_9 independently of one another denote hydrogen or C_1-C_{20}-alkyl,

R_{10} denotes C_1-C_{18}-alkyl, C_6-C_{18}-aryl, C_7-C_{18}-aralkyl or C_2-C_{18}-alkenyl and

n represents a number from 0 to 50,

m represents a number from 1 to 4,

x represents a number from 5 to 100 and

y represents a number from 0 to 100.

Preferred polyether-urethanes are formed by reaction of polymers of ethylene oxide and/or 1,2-propylene oxide, which have been obtained as described above, with a bifunctional isocyanate, such as is described above for the preparation of crosslinked block polymers or copolymers, and a polyalkylenepolyamine.

Polyurea-modified polyether-polyurethanes which have been prepared, for example, from ethylenediamine, diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, polyethyleneimine, 1,2- or 1,3-propylenediamine, dipropylenetriamine, tripropylenetetramine, butylenediamine, hexamethylenediamine, 2,5-diamino-2,5-dimethylhexane, 2,2,4- or 2,4,4-trimethyl-1,6-hexanediamine, cyclohexanediamine, isophoronediamine, hydrogenated toluylenediamines and hydrogenated diaminodiphenylmethanes can also be employed.

Polyamines which are trifunctional or more than trifunctional are preferred here. Diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine are particularly preferred.

Industrial distillation residues from the preparation of the oligoethyleneamines mentioned are also particularly suitable for the preparation of polyurea-modified polyurethanes which can be used according to the invention. These residues then additionally contain branched and/or cyclic polyalkylenepolyamines.

Alkylbenzenesulphonic acid salts which are suitable for the process according to the invention are, for example, salts of alkylbenzenesulphonic acids and alkylnaphthalenesulphonic acids. Salts of dodecylbenzenesulphonic acid are particularly preferred.

It is possible and sometimes advantageous to use a

mixture of 2 or more of the breakers to be employed according to the invention.

The breakers to be used according to the invention can be employed, for example, in an amount of 5 to 18,000 ppm, based on the emulsion to be broken. This amount is preferably 10 to 10,000 ppm.

The water-in-oil emulsion to be broken secondarily according to the invention, which is an oily phase originating from the primary breaking of an oil-in-water emulsion, can originate from the most diverse oil-in-water emulsions, for example from effluents containing fat and/or oil or from used oil-in-water emulsions. Examples which may be mentioned are: mineral oil-based and semi-synthetic cooling, lubricating and rolling oil emulsions, effluents from tank cleaning, bilge water, slop oils, oil-containing wash liquors, degreasing baths to be disposed of, paintshop effluents, oil-containing condensates and effluents from the processing of animal and plant products, from breweries and distilleries, from metalworking and metal processing plants, from membrane processes, for example retention products from ultra-filtrations and reverse osmosis processes, and from flotation processes.

The process according to the invention can be carried out, for example, at temperatures in the range from 0 to 100°C. It is preferably carried out in the range from 10 to 80°C.

The process according to the invention allows substantial dehydration, by secondary breaking, of oily phases which have been obtained from the breaking of oil-in-water emulsions. As a rule, 60 to 90% by weight of the water contained in the oily phases can be removed in the manner according to the invention. Oily phases treated in this way can be worked up and burned more easily and dumped in a better manner than the oily phases which still have a relatively high water content, containing, for example, 20 to 80% by weight of water, which originate directly from the breaking of oil-in-water emulsions.

Examples

The following secondary breakers were used in the examples:

Ethylene oxide/1,2-propylene oxide polymers

A1

A polyether having an OH number of 28 was obtained by alkoxylation of trimethylolpropane (as the starting substance) with initially 80 parts by weight of propylene oxide and then 20 parts by weight of ethylene oxide. The product was adjusted to an active compound content of 45% by weight with toluene. A low-viscosity, almost colourless clear solution was obtained.

A2

A polyether having an OH number of 47 was obtained by

alkoxylation of ethylenediamine with initially 88 parts by weight of propylene oxide and then 12 parts by weight of ethylene oxide. The product was adjusted to an active compound content of 45% by weight with toluene. A low-viscosity, almost colourless clear solution was obtained.

Oxyalkylated phenolic resins

B1

220 parts by weight of nonylphenol and 37 parts by weight of aqueous formaldehyde solution were heated and the mixture was reacted with 4.5 parts by weight of 56% strength sodium hydroxide solution to give a base resin, the water formed being distilled off. 1.4 parts by weight of powdered KOH were then added to 103 parts by weight of the base resin, and the mixture was heated to 148°C and reacted with 78 parts by weight of ethylene oxide. After cooling, the product was rendered neutral with 3.5 parts by weight of acetic acid.

The resulting product was adjusted to an active compound content of 45% by weight with toluene. A clear, slightly yellowish solution was obtained.

Crosslinked polymers of ethylene oxide and 1,2-propylene oxide

C1

36 parts by weight of a bifunctional polyether prepared as described under A2 were reacted with 0.8 part by

weight of potassium tert.-butylate and 1.56 parts by weight of toluylene diisocyanate at 130°C. After subsequent neutralisation with acetic acid and filtration, the product was adjusted to an active compound content of 45% by weight with toluene.

C2

The procedure was as for C1, but instead of toluylene diisocyanate, 1.52 parts by weight of the bisglycidyl ether of bisphenol A were reacted. After subsequent neutralisation and filtration, the product was adjusted to an active compound content of 45% by weight with toluene.

Crosslinked block polymers or copolymers of ethylene oxide and/or 1,2-propylene oxide

D1

Two different solutions were added dropwise to 51.6 parts by weight of toluene:

Solution 1: 0.035 part by weight of toluylene diisocyanate in 22 parts by weight of toluene

Solution 2: 7.6 parts by weight of aminopolyether, which was an amination product of a polypropylene oxide which had been started from trimethylolpropane and had an OH number of 32, in 68.4 parts of toluene.

The solutions were simultaneously added dropwise at the same rate at a temperature in the range from 0 to 5°C. The mixture was then allowed to after-react at room temperature for 2 hours. A pale yellow liquid was obtained.

Polyether-urethanes

E1

15.7 parts by weight of toluylene diisocyanate and 0.02 part by weight of dibutyltin dilaurate were added to a solution of 235.9 parts by weight of a polyether which had an OH number of 21.4 and had been prepared by reaction of butanol with equal amounts by weight of ethylene oxide and propylene oxide, and the mixture was stirred at 50°C until the polyether had reacted completely. This was checked via the isocyanate number. 3 parts by weight of diethylenetriamine were then added at 50°C and the mixture was allowed to after-react at 30°C for 8 hours. A pale yellow liquid was obtained.

Alkylbenzenesulphonic acid salts

F1

52 parts by weight of dodecylbenzenesulphonic acid, 31 parts by weight of xylene and 10 parts by weight of butyldiglycol were brought together at 30°C, and 7 parts by weight of diethylenetriamine were added dropwise to this mixture. The product had a yellowish coloration.

Example 1

An effluent originating from car production which was an oil-in-water emulsion was subjected to primary breaking by addition of 0.1% by weight of a polyamidoamine. The oily phase obtained by this operation, which still contained 40% by weight of water, was broken at room temperature using 0.9% by weight of a secondary breaker. The secondary breaker consisted of a mixture of A1, B1 and C1 in a weight ratio of 1.2:2:2. After 2/4/8/16 hours, 16/20/35/50% by weight of the water present in the oily phase removed had been separated off. A blank sample, that is to say a sample of the oily phase left to stand without addition of a secondary breaker, showed no water separated off after 16 hours.

Example 2

An effluent originating from car production which was an oil-in-water emulsion was subjected to primary breaking with 0.09% by weight of a polyamidoamine. The resulting oily phase, which still contained 44% by weight of water, was broken at room temperature using various dosages of various secondary breakers. The results can be seen from Table 1. A blank sample, that is to say a sample of the oily phase removed left to stand without addition of a secondary breaker, showed no water separated off after 16 hours.

Table 1

Secondary breaker (in the case of mixtures, the weight ratio is stated)	Dosage (% by weight)	Water separated off (% by weight of the water present) after			
		0.5	1	8	16 hours
A1	0.6	25	30	31	31
A2	0.6	29	29	30	30
B1	0.8	10	21	28	30
A1 + A2 1.2:2	0.8	20	20	23	23
B1 + F1 1:2.5	0.8	20	20	22	22

Example 3

The procedure was as in Example 2, but partly with other dosages and the secondary breaking was carried out at a temperature of 60°C. The results obtained can be seen from Table 2. A blank sample, that is to say a sample of the oily phase left to stand without addition of a secondary breaker, showed no water separated off after 1 hour.

Table 2

Secondary breaker (in the case of mixtures, the weight ratio is stated)	Dosage (% by weight)	Water separated off after 1 hour (% by weight of the water present)
A1	0.6	40
A1 + A2 1.2:2	0.6	39
B1 + F1 1:2.5	0.6	40

Example 4

An effluent originating from car production which was an oil-in-water emulsion was subjected to primary breaking with 0.2% by weight of a polyamine. The oily phase obtained by this procedure, which still contained 52% by weight of water, was broken at 80°C using various secondary breakers. The results can be seen from Table 3. A blank sample, that is to say a sample of the oily phase left to stand without addition of a secondary breaker, showed no water separated off after 2 hours.

Table 3

Secondary breaker (in the case of mixtures, the weight ratio is stated)	Dosage (% by weight)	Water separated off after 2 hours (% by weight of the water present)
B1	1	19.2
B1 + F1 1.5:3.5	1	67.3
F1	1	38.5

Example 5

An effluent originating from steel production which was an oil-in-water emulsion was subjected to primary breaking with 0.15% by weight of a polyamine. The oily phase obtained by this procedure, which still contained

60% by weight of water, was broken at 60°C using in each case 0.5% by weight of various secondary breakers. The results can be seen from Table 4. A blank sample, that is to say a sample of the oily phase left to stand without addition of a secondary breaker, showed no water separated off after 2 hours.

Table 4

Secondary breaker (in the case of mixtures, the weight ratio is stated)	Water separated off after x hours (% by weight of the water present) x = 1	x = 1.5	x = 2
B1	0	10	60
A1	0	0	40
B1 + F1 1.5:3.5	10	20	50
B1 + F1 1.5:7.0	25	30	40

Example 6

An effluent originating from steel production which was an oil-in-water emulsion was subjected to primary breaking with 0.18% by weight of a polyamidoamine. The oily phase obtained by this procedure, which still contained 72% by weight of water, was broken at room temperature using in each case 1.0% by weight of various secondary breakers. The results can be seen in Table 5.

A blank sample, that is to say a sample of the oily phase left to stand without addition of a secondary breaker, showed no water separated off after 14 hours.

Table 5

Secondary breaker (in the case of mixtures, the weight ratio is stated)	Water separated off after x hours (% by weight of the water present) x = 1	x = 14
A1	59	60
B1	72	76
A1 + F1 1:1	83	94
B1 + F1 1:2.5	72	90

Example 7

An oil-in-water waste emulsion from the field of waste oil treatment was subjected to primary breaking with 0.4% by weight of a polyamine. The oily phase obtained by this procedure, which still contained 72% by weight of water, was broken at 40°C using 1.0% by weight of various secondary breakers. The results can be seen from Table 6.

Table 6

Secondary breaker	Water separated off after x hours (% by weight of the water present)			
	x = 1	x = 3	x = 5	x = 12
A1	11	18	21	25
A2	11	65	71	83
C2	0	0	60	60

Example 8

The procedure was as in Example 4, but the secondary breakers employed were types C1, D1 and E1. The results can be seen from Table 7.

Table 7

Secondary breaker	Water separated off after x hours (% by weight of the water present)			
	x = 1	x = 3	x = 5	x = 12
C1	4	7	9	10
D1	2	6	13	16
E1	5	11	20	25

What is claimed is:

1. A process for the breaking of water-in-oil emulsions which have been obtained from the breaking of oil-in-water emulsions, in which process breakers are employed selected from the group consisting of polymers and oligomers of ethylene oxide and 1,2-propylene oxide, oxyalkylated phenolic resins, block polymers and copolymers of ethylene oxide and 1,2-propylene oxide crosslinked with diisocyanates, dicarboxylic acids, formaldehyde and diglycidyl ethers, polyether-urethanes and alkylbenzene-sulphonic acid salts.

2. The process of Claim 1, in which polymers obtained by polyalkoxylation of lower alcohols or lower amines are employed as the polymers of ethylene oxide and 1,2-propylene oxide.

3. The process of Claim 1, in which the oxyalkylated phenolic resins employed are those which have been obtained by condensation of alkylphenols with formaldehyde, formalin solution or paraformaldehyde and subsequent alkoxylation.

4. The process of Claim 1, in which the block polymers and copolymers of ethylene oxide and 1,2-propylene oxide crosslinked with diisocyanates, dicarboxylic acids, formaldehyde and diglycidyl ethers which are employed are those which are obtained when a difunctional polyether which consists of 30 to 90 parts by weight of 1,2-propylene oxide and 70 to 10 parts by weight of ethylene oxide and have an average molecular weight

of 2000 to 20,000 are reacted with a bifunctional isocyanate, a bifunctional carboxylic acid, formaldehyde and/or a bifunctional glycidyl ether.

5. The process of Claim 1, in which urea-modified polyether-urethanes of the formula (III)

$$\begin{array}{l} NH\text{-}CO\text{-}NH\text{-}R_3\text{-}[\text{-}NH\text{-}CO\text{-}O\text{-}(CHR_6\text{-}CHR_7O)_x\text{-}(CHR_8\text{-}CHR_9\text{-}O)_y\text{-}R_{10}]_m \\ | \\ R_1 \\ | \\ N\text{-}CO\text{-}NH\text{-}R_4\text{-}[\text{-}NH\text{-}CO\text{-}O\text{-}(CHR_6\text{-}CHR_7O)_x\text{-}(CHR_8\text{-}CHR_9\text{-}O)_y\text{-}R_{10}]_m \\ | \\ R_2 \\ | \\ NH\text{-}CO\text{-}NH\text{-}R_5\text{-}[\text{-}NH\text{-}CO\text{-}O\text{-}(CHR_6\text{-}CHR_7O)_x\text{-}(CHR_8\text{-}CHR_9\text{-}O)_y\text{-}R_{10}]_m \end{array}$$

(III)

in which

R_1 and R_2 independently of one another denote C_2-C_{14}-cycloalkylene,

R_3, R_4 and R_5 independently of one another denote optionally substituted alkylene, cycloalkylene or arylene,

R_6, R_7, R_8 and R_9 independently of one another denote

hydrogen or C_1-C_{20}-alkyl,

R_{10} denotes C_1-C_{18}-alkyl, C_6-C_{18}-aryl, C_7-C_{18}-aralkyl or C_2-C_{18}-alkenyl and

n represents a number from 0 to 50,

m represents a number from 1 to 4,

x represents a number from 5 to 100 and

y represents a number from 0 to 100,

are employed as the polyether-urethanes.

6. The process of Claim 1, in which linked and amine-modified polyalkylene oxides of the general formula (I)

$$\begin{array}{l} NH\text{-}CHR\text{-}(CH_2)_x\text{-}CHR\text{-}[\text{-}OCHR\text{-}(CH_2)_x\text{-}CHR\text{-}]y\text{-}(OCHR\text{-}CHR)_y\text{-}O\text{-}Q\text{-}A \\ | \\ M \\ | \\ NH\text{-}CHR\text{-}(CH_2)_x\text{-}CHR\text{-}[\text{-}OCHR\text{-}(CH_2)_x\text{-}CHR\text{-}]y\text{-}(OCHR\text{-}CHR)_y\text{-}O\text{-}Q\text{-}A \end{array}$$

(I)

in which

each R independently denotes hydrogen or a C_1-C_{20}-

alkyl radical,

each x independently denotes zero or an integer from 1 to 12,

each y independently denotes zero or an integer from 1 to 120,

each Q independently denotes a C_6-C_{18}-arylene, C_7-C_{18}-aralkylene or C_2-C_{18}-alkylene group,

each A independently denotes hydrogen, hydroxyl or a radical of the formula (II)

$$-(OCHR\text{-}CHR)_y\text{-}[\text{-}OCHR\text{-}(CH_2)_x\text{-}CHR\text{-}]_y\text{-}OCHR\text{-}(CH_2)_x\text{-}CHR\text{-}NH_2 \quad \text{(II)}$$

where R, x and Y are as defined above, and

M denotes the radical of a diisocyanate, a bis-epoxide, a dicarboxylic acid, a dicarboxylic acid dihalide, a biscarboxylic acid anhydride, a diester or a dihalogen compound, after the two reactive groups in each case have reacted with an amine hydrogen atom,

are employed as the polymers of ethylene oxide and/or 1,2-propylene oxide.

7. The process of Claim 1, in which 5 to 18,000 ppm of breaker, based on the emulsion to be broken, are employed.

8. The process of Claim 1, which is carried out at temperatures in the range from 0 to 100°C.

9. The process of Claim 1, in which the water-in-oil emulsion to the broken is the oily phase which has been obtained in a primary breaking from effluents containing fat and/or oil or from used oil-in-water emulsions.

Fetherstonhaugh & Co.,
Ottawa, Canada
Patent Agents

SUBSTITUTE

REMPLACEMENT

SECTION is not Present

Cette Section est Absente